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HIGH PRESSURE SYNTHESIS OF STOICHIOMETRIC INDIUM PHOSPHIDE, (U)
SEP 79 T A FAUTH, J A ADAMSKI
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pressurizing, and cooling parameters to safely produce pure, stoichiometric large grain, polycrystalline indium phosphide.

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Contents

1. INTRODUCTION	5
2. BACKGROUND	5
3. PROPERTIES OF INDIUM, PHOSPHORUS, AND INDIUM PHOSPHIDE	7
3.1 Indium—III-A Element	7
3.2 Phosphorus—VA Element	7
3.3 Indium Phosphide—III-V Compound	8
4. SYNTHESIS	9
4.1 Pressure Control	9
4.2 Furnace, Profile, and Ampoule Configuration	10
4.3 Experimental Preparation	12
4.4 Synthesis Procedure	13
5. SUCCESS OF SYNTHESIS	16
6. CONCLUSIONS AND RECOMMENDATIONS	17
REFERENCES	19

Illustrations

1. Vapor Pressure Curve of Solid Red Phosphorus	10
2. Indium Phosphide Synthesis Furnace With Reaction in Progress	11

Illustrations

3. Vacuum/Baking System	13
4. Indium Phosphide Melt Solidification Rate Resulting in Vessel Fracture Due to the Sudden Release of Heat of Fusion of Indium Phosphide at 27.5 Atmospheres Pressure	15

Tables

1. Characteristics of Elemental In and red P, and InP	9
2. Hall Measurements on Polycrystalline InP Synthesized at Full Pressure	16
3. Sources, Form, and Purity of Reactants	17

High Pressure Synthesis of Stoichiometric Indium Phosphide

1. INTRODUCTION

This report discusses a technique developed in this laboratory for the direct reaction of elemental phosphorus and indium for the synthesis of the semiconductor compound indium phosphide and the related problems encountered. Indium phosphide is a group III-V semiconductor compound possessing a direct band gap of 1.35 eV and capable of high carrier mobility depending on the purity of the starting materials, growth technique, and dopants. Increasing interest in indium phosphide has been generated because the compound: (a) is used as a substrate for lattice matched fiber optic sources and detectors in the 1.2 - 1.4 μm wavelength range where commercially available silica fibers have minimum absorption and dispersion; (b) is used for the fabrication of high frequency low noise microwave devices; and (c) has possibilities for the fabrication of high efficiency solar cells.

2. BACKGROUND

Indium phosphide can be synthesized either by direct reaction of elemental phosphorus with elemental indium, or by reactions involving compounds of these elements. The direct reaction has an advantage in that high-purity elements can be

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obtained and there is no possibility of contamination by other reactants or products. The reaction is highly exothermic and, if not properly controlled, can lead to a rapid, even catastrophic, pressure buildup. A number of investigators¹⁻⁵ have used various reactions involving compounds, however, the resulting indium phosphide was insufficiently pure for the growth of high purity single crystals. Direct synthesis from the elements yields the highest purity and largest quantities.

The approach taken in this laboratory is a modification of the following: Using a two zone furnace, the phosphorus is transported in the vapor phase from a stock of solid phosphorus in the low temperature region of an ampoule to a stock of indium in a thermally isolated high temperature region.⁶⁻⁸ This method allows a reaction to occur at a controlled rate without overheating the large mass of phosphorus. Previous attempts to use this sort of direct reaction have been limited to the production of small quantities of indium phosphide.

In the present method, the separate containment of the elements in specific temperature zones, combined with the laboratory established procedures of heating and cooling, eliminated the previous explosion hazards, and increased the volume of material produced from 65 gms to 130 gms.⁹ The volume of indium phosphide is limited primarily by the furnace length and diameter of the heavy walled quartz tubing.

The optimum end result is the determination of the most feasible method for synthesizing indium phosphide which has the following characteristics:

- (1) Low N, (carriers/cm³) at 77°K in the 10¹³ - 10¹⁴ range,
- (2) High μ_e , (cm³/volt-sec) at 77°K in the 9.0×10^4 plus range,
- (3) Short Run-time/Product-weight Ratio.

1. Effer, D., and Antell, G. R. (1960) J. Electrochem. Soc. 107:252.
2. Garton, G., and Powell, H. M. (1957) J. Inorg. Nucl. Chem. 4:84.
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9. Klausutis, N., Adamski, J., and Sampson, J. (1976) Synthesis of Indium Phosphide, In-house Report RADC/TR-76-305.

3. PROPERTIES OF INDIUM, PHOSPHORUS, AND INDIUM PHOSPHIDE

3.1 Indium—III-A Element

Indium is a silvery white metal, brilliant in luster, more malleable than lead, wets glass, and has a face centered tetragonal crystal structure. Indium has three valence electrons and is therefore an electron acceptor and has an electron structure $[Kr] 4d^{10} 5s^2 5p^1$ in the neutral state. Indium is available in many physical forms and purities of which we prefer the ingots of 6N (99.9999 percent) purity.

The indium ingots were purchased in plastic containers sealed in an inert atmosphere and are not opened until needed. Normal handling of the ingots requires the least additional preparation. Indium metal is stable in dry air and has a low order of toxicity such that normal hygienic precautions are sufficient. However, our experience has shown it tends to oxidize (In_2O) when stored in contact with open air, which must be removed by etching and/or baking to preserve the purity. This finding resulted in changing from the use of indium in the tear drop form to the ingot form because of the vast reduction in surface area. In our initial experiments we used 6N indium in tear drop form. Two methods were used to remove the unwanted oxides. Sublimation by vacuum baking at $700^\circ C$ or direct removal by chemical etching using the following procedure:

- (1) Initial etch in concentrated HNO_3 for 5 sec at room temperature,
- (2) Etch in concentrated HCl for 5 sec at room temperature,
- (3) Rinse in methanol at room temperature,
- (4) Rinse in H_2O , (distilled),
- (5) Blow dry with an inert gas.

Indium in ingot form normally did not require oxide removal but was melted into its boat under vacuum.

3.2 Phosphorus—VA Element

Since phosphorus vapors are very toxic, extreme care should be exercised to avoid vapor inhalation and exposure to the skin (absorption). Van Wazer¹⁰ cautions: "At normal temperatures and humidities, red phosphorus reacts slowly with H_2O vapor and O_2 in air to form phosphine (PH_3) and a mixture of the oxyacids of phosphorus. This slow oxidation is exothermic and is accelerated by an increase in temperature..."

Solid phosphorus exists in several allotropic forms. At standard temperature and pressure the element is commercially available as crystalline white phosphorus

10. Van Wazer, J. R. (1958) Phosphorus and Its Compounds, Vol. 1, Interscience Publ. Inc., New York, p. 118.

(cubic α white P), violet phosphorus (violet P), amorphous red phosphorus (red P), and as black phosphorus (black P) which is thermodynamically most stable. White P is extremely toxic and is the most reactive of these (undergoes spontaneous combustion in the presence of O_2 to form the pentoxide P_2O_5). White phosphorus readily converts to amorphous red phosphorus above $350^\circ C$ and into crystalline red phosphorus at $520^\circ C$.¹¹

Similarities are found in the chemistry of phosphorus and carbon in that they form covalent bonds in their compounds, excepting for metallic bonds. Phosphorus has an electron structure of $[Ne] 3s^2 3p^3$ in the neutral state.

Data from Bachmann and Buehler¹² was used for determining the operating temperatures and corresponding pressures of phosphorus and indium phosphide during the synthesis and are discussed later in this report.

The source of red P for the synthesis was commercial lump material of 6N purity available in 25 gm, 50 gm, and 100 gm units. Packaging was in the form of sealed glass ampoules and screw top vials of which the latter was preferred for ease of handling in materials preparation. The sealed glass ampoules were more difficult to work with than the vials because the ampoules were not as simple to open and extra measures were required for temporary storage of the unused portion of red P.

3.3 Indium Phosphide—III-V Compound

Indium phosphide is a III-V semiconductor compound possessing a direct band-gap energy of 1.35 eV ($\lambda = 0.92 \mu m$) and capable of high carrier mobility. The indium phosphide sphalerite crystallochemical structure corresponding to the sp^3 hybridized covalent ionic bond with each atom containing an octet of electrons in its outermost shell. The sphalerite structure yields a coordination number equal to four. An extensive discussion of bond structure, transport and chemical properties, materials characterization and devices is contained in the publication by Kennedy et al.¹³ Table 1 lists the characteristics of elemental indium and red P, and indium phosphide.

11. Bachmann, K.J., and Buehler, E. (1974) J. Electrochem. Soc. 121:838.
12. Bachmann, K.J., and Buehler, E. (1974) J. Electrochem. Soc. 121:835.
13. Kennedy, J.K., Lessoff, H., and Lile, D.L. (1977) InP - An Assessment of United States Activities, In-House Report RADC-TR-77-398.

Table 1. Characteristics of Elemental In and Red P, and InP

	AT No.	AT/MOL Wt	MP °C	BP °C	Oxidation States	Specific Gravity (g/ml)
In	49	114.82	156.61	2080	+1 +3	7.30
Red P	15	30.9738	590	-	$\pm 3 \pm 4 \pm 5$	2.34
InP	-	145.79	$1062 \pm 1^\circ\text{C}$	-	-	4.79

4. SYNTHESIS

4.1 Pressure Control

Bachmann and Buehler¹⁴ have determined the melting point of stoichiometric indium phosphide to be $1062 \pm 1^\circ\text{C}$ and the thermal decomposition pressure to be 27.5 ± 1 atmospheres. Thus 27.5 atmospheres of phosphorus vapor pressure must be supplied at temperatures equal to and just in excess of the melting point of indium phosphide to drive reaction 1 to the right.



This phosphorus pressure prevents decomposition of the newly synthesized indium phosphide but care must be taken to insure that the red P sublimation vapor pressure does not exceed the pressure limit of the synthesis vessel (quartz ampoule). Bachmann and Buehler¹⁵ also measured the vapor pressure of several commercial grades and specially prepared crystalline samples of red P and determined the following equation for calculating the vapor pressure of red P at $P > 10$ atmospheres,

$$\ln P = -(10.8 \pm 0.4) \times 10^3 / T + (16.5 \pm 0.6) \quad (2)$$

where P is in atmospheres and T is in °K. In their paper, Bachmann and Buehler claim that if red P of at least 5N purity is used, then above 450°C , the sublimation pressure calculated from Eq. (2) is accurate to within 10 percent. Utilization of the limits of their equation however greatly exceed 10 percent. Despite this anomaly this equation is, in our opinion, the best available for the calculation of the vapor pressure of red P vs temperature and was used in our experiments to determine the pressure of red P inside our synthesis ampoules. A plot of the equation, exclusive of limits, is shown in Figure 1.

14. Bachmann, K. J., and Buehler, E. (1974) J. Electrochem. Soc. 121:835.

15. Bachmann, K. J., and Buehler, E. (1974) J. Electrochem. Soc. 121:845.

Commercial forms are in the state between the amorphous and monocrystalline forms. We use 6N pure red P to further reduce the limits and the variation from reproducible results.

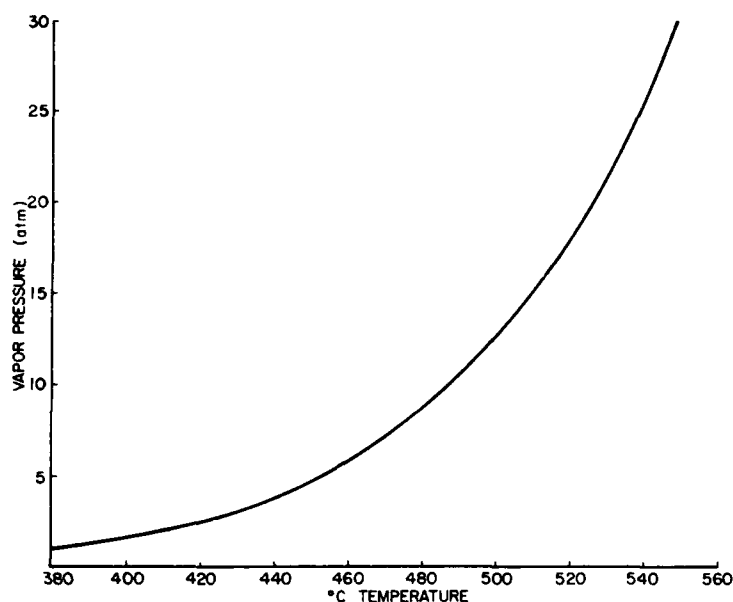


Figure 1. Vapor Pressure Curve of Solid Red Phosphorus

4.2 Furnace, Profile, and Ampoule Configuration

The synthesis furnace consists of two alundum cores wound with Kanthal A-1 resistance wire. The separately wound cores are powered and controlled by Halmar 12 KW SCR power supplies and L&N Electromax III temperature controllers. By inserting an inconel pipe through the furnace cores, flattened profiles are obtained. The Inconel 600 pipe is capable of withstanding the operating temperatures with minimal oxidation. Platinel II thermocouples are used and found to be the most durable for controlling and monitoring the temperatures involved as opposed to chromel alumel thermocouples.

The solid profile in Figure 2 is typical of the one used for our synthesis. The maximum melt temperature in all cases is approximately 1150°C to minimize quartz devitrification and contamination by the reaction of indium with the quartz boat. Temperature fluctuations are further reduced by effectively eliminating cross drafts

through the core by inserting an end cap in the alundum core and using fiberfrax on the red P end as needed. The profile determines the lengths of the ampoule, boat, and melt zone. The length of the melt zone can be increased by adding another winding or series of windings where the end cap is presently located. Inclusion of such a winding resulted in a profile shown by the dashed line in Figure 2. The furnace length, insulation, and isothermal characteristics are the limiting factors for determining the length of the melt zone and in turn the quality of materials synthesized for a particular ampoule diameter.

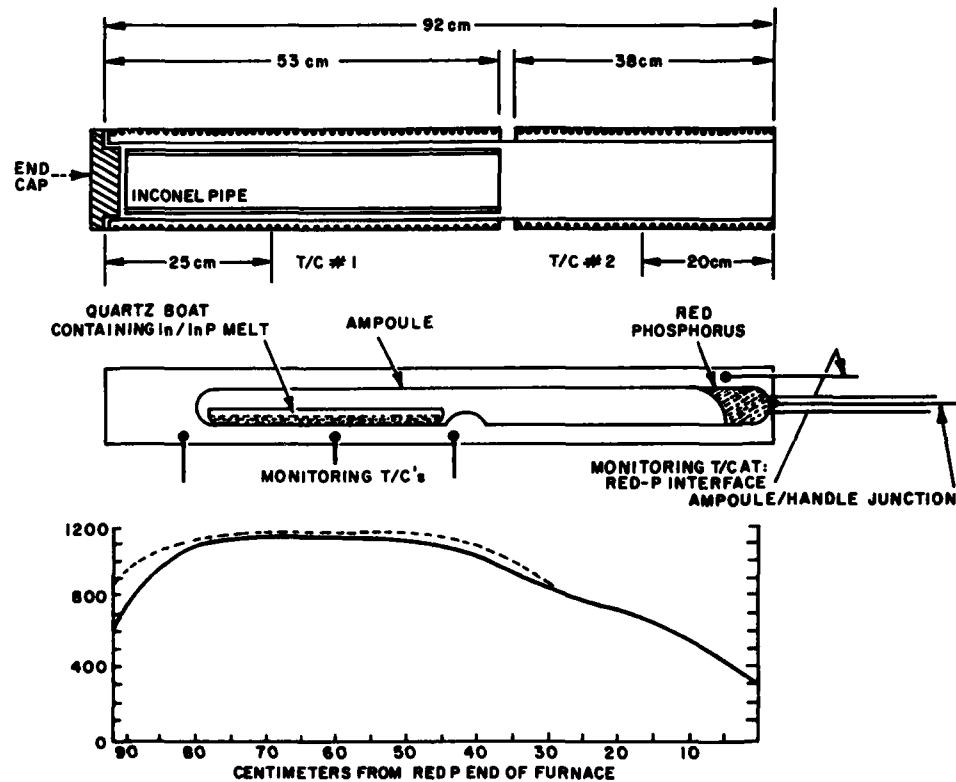


Figure 2. Indium Phosphide Synthesis Furnace With Reaction in Progress

The best of several ampoule designs considered is shown which allows the options of:

- (1) Using a boat and containing any melt spills in the desired temperature zone or,
- (2) Merely containing the melt when not using a boat, as long as the ampoule is not rotated during the synthesis.

The quartz ampoules used are 12.7 mm ID \times 19 mm OD and can safely withstand at least 30 atmospheres of internal pressure.¹⁶ The handles are 6 mm ID \times 8 mm OD quartz tubing fused directly to the ampoule to allow precise temperature monitoring 3 mm from the final red P interface.

4.3 Experimental Preparation

The indium and red P were prepared as previously described in the properties section. Quartz ware is carefully cleaned at room temperatures as follows:

- (1) Aqua regia etch for 3 hours,
- (2) Etch in 10 percent HF solution for 1/2-hour,
- (3) Extensive rinse in voluminous quantities of distilled water,
- (4) Rapid draining and drying in air,
- (5) Bake at 400°C to further remove water.

This procedure effectively removed skin oil contaminants and reduced the possibility of devitrification. Lint-free cotton gloves are worn as standard procedure during handling and fabrication techniques.

First, lump form red P is loaded (after weighing) into the vertically positioned ampoule. Second, the quartz boat (if used) containing the indium is placed inside the horizontally positioned ampoule. Three sorption pumps and a Vacion pump are used for evacuating the ampoule (as shown in Figure 3) prior to sealing with an oxygen-hydrogen torch. Typically, an ampoule is evacuated to $\leq 5 \times 10^{-7}$ torr prior to sealing. Red P outgassing prevents reaching much lower pressure.

The phosphorus vapor exists as P_4 at $T \leq 800^\circ\text{C}$. A small indefinitely determined increasing percentage of P_2 exists at $T > 800^\circ\text{C}$.¹⁷ Since our pressure controlling temperature is 545.9°C the calculation for stoichiometry and vapor pressure was based upon the P_4 molecule and the total unoccupied volume, $V_{t. u.}$, inside the ampoule determined by

$$V_{t. u.} = V_{\text{ampoule}} - V_{\text{quartz boat}} - V_{\text{In}} - V_{\text{red P}} \quad (3)$$

A typical set of values are 100 gms indium, 30 gms red P to react with the indium stoichiometrically and provide the overpressure of 27.5 atmospheres of phosphorus vapor.

16. Friel, J. (1977) General Electric - Private Communication.

17. Van Wazer, J. R. (1958) Phosphorus and Its Compounds, Vol. 1, Interscience Publ. Inc., New York, p. 95.

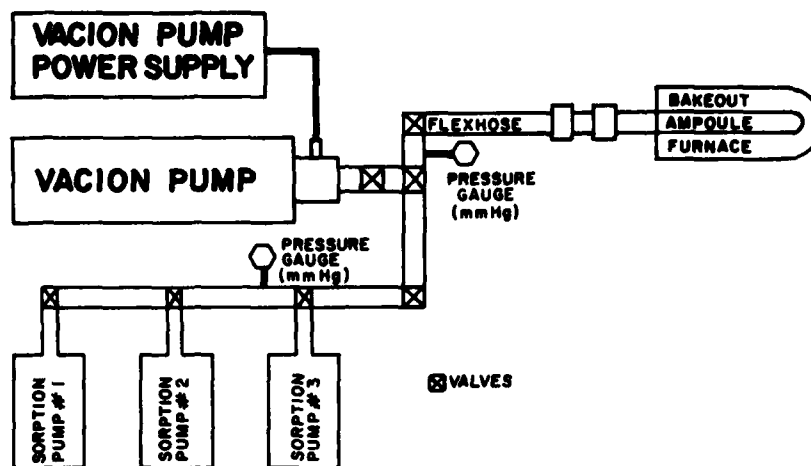


Figure 3. Vacuum/Baking System

4.4 Synthesis Procedure

This procedure for synthesizing stoichiometric indium phosphide has solved the explosion problem which has been known to occur when operating at full pressure.¹⁸ We found that excess indium in the indium rich indium phosphide zone wets to and cracks the quartz upon expansion and solidification during the cooling cycle. The high pressure from the phosphorus then explodes the ampoule because of the weakened wall. Our indium phosphide product is stoichiometric, does not wet to the quartz in any way, and is resultantly easily removed from the boat or ampoule.

Specifically, the process is composed of two series of steps:

- (1) Temperature control from time $t = T_i$ to reaction completion,
 - (2) Temperature control for cooling to room temperature, time $t = T_f$.
1. Temperature Control from time $t = T_i$ to reaction completion.
 - (a) First, the temperature of the indium is raised to between 1062°C and 1150°C, and kept there until the cool-down procedure begins.
 - (b) Simultaneously, the temperature of the red P is brought up to a maximum of 380°C, which yields about 1 atmosphere of pressure according to the lower extreme of the vapor pressure curve.
 - (c) The temperature of the red P is raised slowly until the interface temperature reads 546°C (27.5 atmospheres pressure) which causes two actions to occur:

18. Klausutis, N., Adamski, J., and Sampson, J. (1976) Synthesis of Indium Phosphide, In-House Report RADC-TR-76-305, p. 12.

- (1) Some of the red P will react with the molten indium,
- (2) The rest of the red P will be completely compacted in the cold end of the ampoule.

Note: T_i = initial time, run begins,

T_f = final time, run completed.

- (d) The interface is moved slowly into the furnace by moving the entire ampoule (and still maintaining the indium/indium phosphide melt in the 1062 - 1150°C zone) such that the interface remains at 546°C. When the red P is completely sublimed, the synthesis is complete. However, one hour of soak time is often added to insure complete reaction.
2. Temperature control for cooling to room temperature, time $t = T_f$.
- (a) While at full pressure of 27.5 atmospheres, the temperature of the indium phosphide is decreased from 1150°C MAXIMUM to 1050°C at rates of between 50°C/hr and 150°C/hr. This allows the melt to solidify while maintaining the vapor pressure to prevent decomposition of the indium phosphide product.
 - (b) The temperatures of both the indium phosphide and red P are decreased simultaneously at rates of between 60°C/hr and 150°C/hr, and 90°C/hr and 180°C/hr, respectively until the red P zone reaches 380°C and the indium phosphide zone reaches 750°C.
 - (c) When the temperature of the red P end of the ampoule reaches 380°C (1 atmosphere red P pressure) and the indium phosphide end reaches 750°C the power to the furnaces is turned off and the ampoule, product, and red P cool to room temperature "in situ."

The limits for the cooling rates were established experimentally. Slower cooling rates result in unfractured material. If rates much faster than those given are used, then chances of success are severely limited because of the heat of fusion of indium phosphide.

The product cools from both ends of the melt zone toward its middle as the cooling procedure is followed. Decreasing the temperature of the indium phosphide too rapidly results in a large release of heat of fusion in a very short time. The thick-walled quartz tubing and furnace lagging does not allow the heat transfer to occur as efficiently as desired. Because the pressure is still at 27.5 atmospheres during the initial part of the cooling procedure to maintain stoichiometry, the heat is transferred throughout the interior of the ampoule and effectively raises the temperature in the red P section of the ampoule. An increase in temperature in this section also raises the pressure inside the ampoule. An explosion will occur

if the pressure exceeds the limits of the ampoule (551°C - 30 atmospheres) as is shown with one specific case in Figure 4. (Bachmann and Buehler also observed a similar effect.¹⁹⁾

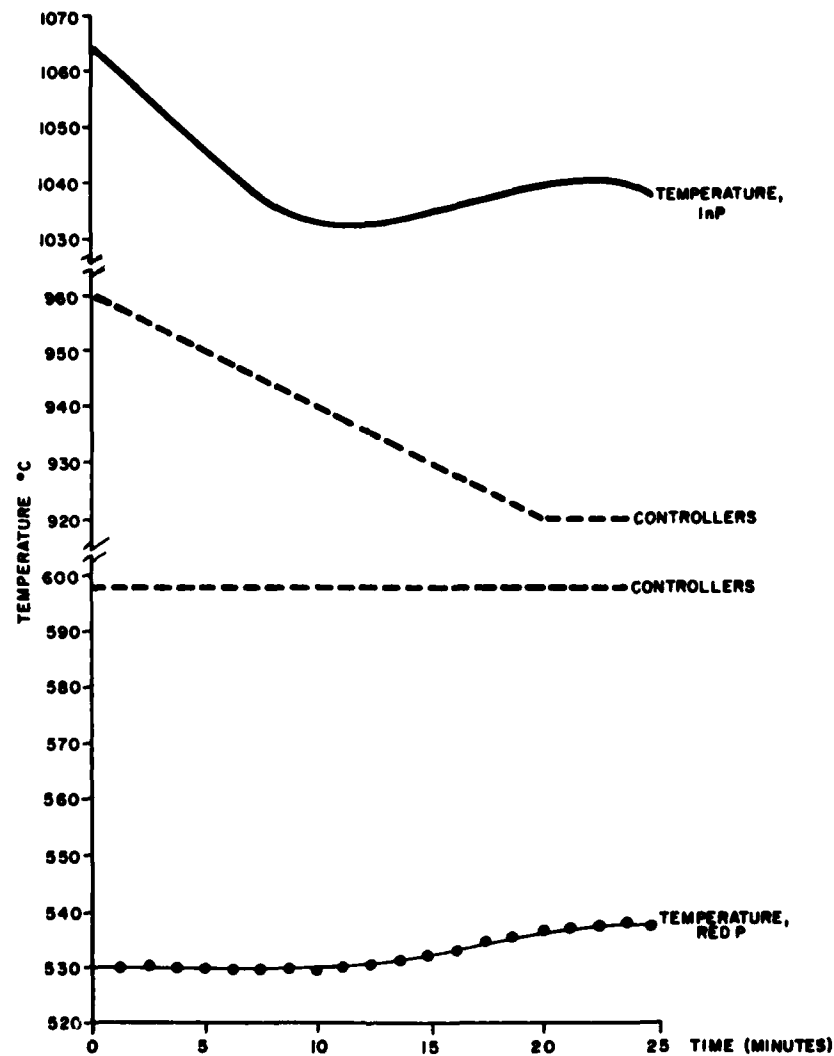


Figure 4. Indium Phosphide Melt Solidification Rate Resulting in Vessel Fracture Due to the Sudden Release of Heat of Fusion of Indium Phosphide at 27.5 Atmospheres Pressure

19. Bachmann, K.J., and Buehler, E. (1974) J. Electrochem. Soc. 121:843.
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5. SUCCESS OF SYNTHESIS

Successful synthesis of indium phosphide from the elements indium and phosphorus has repeatedly been accomplished using the laboratory investigated technique presented which has solved the explosion problem. The reaction is conducted in the 1062°C - 1150°C temperature range and at 27.5 atmosphere sublimation vapor pressure. Reactants must be of 6N purity and all quartz ware must be thoroughly cleaned and handled with lint-free cotton gloves.

The primary limitations are:

- (1) The diameter of the quartz tubing fabricated to take at least 30 atmosphere pressure.
- (2) The shape of the profile and in turn the length of the melt zone.
- (3) Manual operation of the equipment.

Polycrystalline ingots of indium phosphide weighing up to 130 gms have been synthesized from the elements at 27.5 atmospheres in thick walled quartz tubing. Large single crystal grains (up to 1 cm² as determined by Laue back reflection X-ray technique) were characterized by Hall measurements using the Van der Pauw technique (Table 2). Table 3 shows the vendor sources, form, purity of reactants and synthesized quantities produced.

Table 2. Hall Measurements on Polycrystalline InP Synthesized at Full Pressure

Sample	$N_D - N_A$ (cm ⁻³)		Mobility 300°K	(cm ² /V-sec) 77°K
	300°K	77°K		
6, 7, 8 (LEC)	3.9×10^{15}	3.5×10^{15}	3880	15,610
15	1.2×10^{15}	8.0×10^{15}	3270	9690
16	1.0×10^{16}	6.3×10^{15}	4830	9420
17	1.3×10^{16}	9.8×10^{15}	3360	11,520
18	7.4×10^{15}	5.5×10^{15}	3270	13,500
19	2.5×10^{15}	1.6×10^{16}	3650	13,440
19 (LEC)	2.0×10^{16}	1.3×10^{16}	3490	6740
21	2.8×10^{15}	2.3×10^{15}	4295	25,810
25	4.4×10^{15}	3.5×10^{15}	4280	25,220

Table 3. Sources, Form, and Purity of Reactants

Run	In	Purity Form	red P	Purity	Grams
6 no boat	Ventron	6N/tear drops	Ventron	6N	38
7 "	Ventron	"	"	"	63
8 "	In Corp. of Am	"	"	"	51
15 boat	"	5N/Wire	"	"	75
16 "	"	"	Puratronic	"	75
17 "	"	"	"	"	115
18 "	"	"	"	"	115
19 "	Puratronic	6N/Ingots	"	"	125
21 "	Metal Specialties	"	Metal Specialties	"	126
23 "	"	"	Puratronic	"	130
25 "	Puratronic	"	Metal Specialties	"	126

6. CONCLUSIONS AND RECOMMENDATIONS

The high pressure indium phosphide synthesis technique described in this report has been used to produce meaningful quantities of indium phosphide and in the author's opinion can be readily scaled up to synthesize larger quantities by increasing the charge length and/or the ampoule diameter. Replacing our inconel pipes with isothermal furnace liners (heat pipe) would produce isothermal zones for both the indium and phosphorus which would maintain large zone lengths to $\pm 1/2^\circ\text{C}$ and greatly reduce the danger of overheating.

The highest purity indium phosphide synthesized to date using this technique had a carrier concentration of 2.3×10^{15} carrier/cm³ and a mobility of 25,810 cm²/V-sec at 77°K. Even this material did not meet our ultimate purity objective although it is sufficiently pure to be used for the growth of single crystals for substrates for fiber optic sources and detectors, FET's or solar cell's. In our opinion based on other low temperature solution growth of indium phosphide at low phosphorus pressure the most likely source of contamination is the reaction of indium with its quartz container at the high temperatures used. Two possible solutions are suggested to reduce this problem. First the use of a less reactive boat material such as pyrolytic boron nitride and second reducing the length of time that the indium/indium phosphide melt is at elevated temperature. The time required for synthesis at the melting point of indium phosphide and at full pressure is very short, < 1 hour. The 2-3 days required to complete the runs described above were necessary to prevent overheating and eliminate explosions. The low run-time/product weight ratio requirement was met.

While as stated above, we feel that the high pressure technique for the synthesis of indium phosphide as outlined in this report is scalable, the ability of available quartz ware to withstand the necessary 27.5 atmosphere pressure is always an uncertainty due to fabrication problems in maintaining the necessary wall thickness. The problem of containing the high pressures involved could be eliminated by placing the entire furnace assembly inside a high pressure chamber. In this instance the quartz ware would only have to withstand the internal-external pressure differential. If such a system could also be equipped with an auxilliary traveling heater which could produce a short zone of material at the melting point of indium phosphide, then while the remainder of the ampoule is maintained at 546°C (to maintain the necessary 27.5 atmospheres of red P) synthesis could be achieved in the zone as it traveled. In such a system the high temperature portion of the melt would be exposed to its container for the very short time required for synthesis; < 1 hour.

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